

CAPP

International Research Project on the Effects of Chemical
Ageing of Polymers on Performance Properties

1N-27-CR
078951

**CORRELATION OF CHEMICAL AND
PHYSICAL TEST DATA FOR THE
ENVIRONMENTAL AGEING OF
TEFZEL (ETFE)**

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Document no: CAPP/M.13 Rev A

Document date: 4 December 1996
Revised 25 February 1997

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SYNOPSIS

Data from the many different tests conducted on Tefzel by MERL and TRI during Phase 1 of the CAPP project are reviewed herein with the objectives of identifying any trends or correlations between them. This report applies a similar approach to that in CAPP/M.10, which performed this task for Coflon. Some discussion on underlying mechanisms is included, and a rationale for the overall behaviour is suggested.

No evidence has been found to date that Tefzel degrades chemically when immersed at either high or ambient pressures, and at high temperatures, in any of the project fluids A, B, F, G and I. However, physicochemical effects are identified, although none of these has demonstrated deterioration at a catastrophic rate; any property losses occur over a reasonable period of time at elevated temperatures. Unlike Coflon, Tefzel is more likely to exhibit reduced properties in aromatic oil than in methanol, and may exhibit minuscule fracturing due to explosive decompression.

All of the ageing effects have resulted in increases in high pressure gas permeation rates, especially with Fluid I.

1 INTRODUCTION

In a similar approach to that used for the previously issued correlation report for Coflon (CAPP/M.10), this report aims to identify any correlations between mechanical property changes and chemical/morphological changes for Tefzel, using information supplied in other MERL and TRI project reports. Differences identified with Coflon behaviour will be of scientific interest as well as appropriate to project applications, as Tefzel and Coflon are chemical isomers.

Owing to the considerable chemical resistance of Tefzel, much of its testing so far has been based on mechanical properties. Where changes have occurred, chemical analysis can now be targeted more effectively.

Relevant test data collated here include: tensile modulus and related properties, permeation coefficients, % crystallinity, some crack growth resistance measurements, and other observations where significant.

Fluids based on methanol and amine (Fluid G), a mixture of methane, carbon dioxide and hydrogen sulphide gases plus an aqueous amine solution (Fluid F), and an aromatic oil mix of heptane, cyclohexane, toluene and 1-propanol (Fluid I) have affected Tefzel to varying degrees, and are discussed in some detail herein.

2 COMMENT

The major use of Tefzel (ETFE) in offshore oil production is as umbilicals. Hence its chemical resistance to methanol is of particular importance. Other umbilical materials are: Hytrel, which has suffered stress crazing under some conditions, and Nylon 11. One possible reason why Tefzel has not been employed for flexible pipes thus far is its tendency (unlike Coflon) to fracture internally ('craze') during explosive decompression testing. Although such tests have not been a direct part of the CAPP project, this observation was originally made when removing testpieces generally from the various high pressure gas exposures, until the procedure was altered to avoid it.

The inherent chemical inertness of ETFE is such that, to date, a suitable solvent has not been found to make the solutions necessary for GPC measurements. Hence assessment of any chemical changes which alter molecular weights has been impossible. X-ray diffraction studies are beginning to reveal changes in crystallinity due to ageing. However, most of the data generated so far have been from mechanical properties.

3 RESULTS AND DISCUSSION

Unlike Coflon, Tefzel can be easily processed without the need for plasticizer. This should make the definition of baseline unaged Tefzel properties a great deal easier and, in the main, does so. However, TGA work has shown that the first 2% of Tefzel weight loss during this technique is associated with a lower activation energy than the remainder (although the value was still high); 2% of low molecular weight material was thus inferred. As will be seen, this low molecular weight species (modifier - perhaps termonomer) is apparently leached out during ageing in an analogous way to plasticizer loss for Coflon. Consequent effects on properties are addressed in this review.

Effects of exposures to the various fluids employed are now reviewed in turn for Tefzel. Those fluids which might be expected to react chemically with Tefzel are considered before those where only physical or physicochemical effects might be anticipated. In general, the comments concerning comparisons across tests made in section 2 of CAPP/M.10 also apply for comparisons made herein. More specifically, for expediency most of these have involved tensile test data, although more information might be expected from dynamic fatigue tests: however, the time required for the latter, and the initial lack of 6mm thick material for samples, have restricted the number of tests conducted. Where they have been performed, crack growth resistance (CAPP/M.10) has been used to quantify each set of results in a single value for comparison purposes.

Tensile test values (obtained at 23°C throughout) are useful for assessments of property changes (e.g. for modulus) brought on by exposure to a fluid, but they should not be compared directly with Coflon values elsewhere because Tefzel testpieces were only half the thickness of Coflon specimens, and thickness is known to affect tensile behaviour.

Tefzel possesses a glass transition temperature T_g (applying to its amorphous layer) of ca130°C.

3.1 Fluid F (wet H₂S gas mixture and amine)

Fluid F is: 94/5/1 CH₄/CO₂/H₂S gases saturated with water vapour, the water originally-added containing 1% of ethylene diamine. All exposures were carried out in the vapour phase of the mixture.

Table 1 summarises the property and analytical results for Fluid F 5000psi exposures of Tefzel at a variety of temperatures and test durations, and Figures 1 to 3 plot some of the tensile modulus (1%) data from this table, for exposure temperatures 100C, 120C and 140C respectively.

140C exposures

After about 1 week's exposure, clear evidence of a minimum modulus value 25% lower than the original is shown in Figure 3. Factors which could cause the initial softening stage are

- loss of crystallinity (26%→20%)
- relatively high concentration of gas absorbed (as supported by the concentration value (albeit at 150C) from high pressure CH₄ permeation testing through unaged Tefzel - see footnote, Table 1).

During the subsequent 3 week exposure, the modulus increased again, essentially to its original value. This has in the past been attributed to loss of low molecular weight species, as evidenced by TGA measurements early in the project: as this species leaves, partial collapse of the morphological structure at 5000psi would lead to stiffening. The accompanying 66-100% increases in HP CH₄ permeation rates through aged samples presumably arises because there is more amorphous region to permeate through (from the crystallinity loss), and/or perhaps also from (i) contributions from internal flaws which have occurred due to the removal of low molecular weight species, (ii) minuscule explosive decompression fracturing effects, occurring as the exposure period is ended.

The unchanging elemental analysis value for % fluorine present strongly suggests that no crosslinking is occurring: the stiffening stage is probably not occurring for a chemical reason. (To confirm this, GPC measurements - not possible for Tefzel because no appropriate solvent has been found - would be required.)

120C exposures

The same pattern for change in modulus with exposure time is indicated, albeit less clearly, after 120C exposures (see Figure 2). Once again, a minimum value is reached before the modulus increases again towards its original unaged value, although there is some variation near the minimum.

Crystallinity levels were again reduced after 4 weeks at 120°C, to 22.9% compared to 26% for the unaged material. Methane permeation at 150C and 5000 psi had increased by 66% after 4 weeks at 120C.

The modulus reduction to the minimum was not so great as that at 140C, probably reflecting the lower crystallinity loss and reduced gas concentration value at 120C.

100C exposures

The presence of a modulus minimum as discussed above is again indicated (Figure 1), but to a slight degree only, despite the considerable crystallinity loss observed (26%→18%), and a reasonable concentration of absorbed gas. The contribution of losing low molecular weight species apparently manifests itself relatively more quickly at 100C than at the higher temperatures. HP CH₄ permeation rates through aged samples are again 50-100% greater than through unaged Tefzel.

85C exposures

Tensile data for 85C exposures are also shown in Table 1. Modulus reductions have occurred, but the minimum was not reached after 6 months.

General

Factors other than modulus measured during tensile testing have remained reasonably constant throughout this ageing exercise. Ultimate strain has varied the most, but always at high values.

As modulus dropped to a minimum value at 100C, 120C and 140C, plotting log reciprocal time to this minimum against reciprocal absolute temperature could give a straight line relationship. The plot obtained (Figure 4(a)) was approximately linear, with an activation energy of 9kcal/mol. It is likely that the 1/t 120C value should be greater (cf time variation

around the minimum in Figure 2), so this activation energy is probably reasonably representative, but perhaps slightly low. This value indicates that the change is probably not of a chemical nature, which would agree with the reasoning above, viz, initial reduction in modulus may be related to losses in crystallinity or gas absorption. However, the situation is perhaps more complex than this, as discussed in the last paragraph of this section.

Due to insufficient results at 100C, no analogous Arrhenius plot was obtained for the second stage, the subsequent increase in modulus which is sensibly associated with the slow loss of the 2% of low molecular weight species present. Insufficient X-ray diffraction data are available to substantiate this picture more fully by obtaining similar Arrhenius plots from the diffraction results. More values at longer times for each of the temperatures (and at a shorter time for 120C) would be necessary.

The two crack resistance measurements - obtained for unaged and well-aged (4 weeks 140C) testpieces - were very similar (as were the mechanical properties for these testpieces).

The observations above, plus the similar elemental analysis values for % fluorine and the lack of change in appearance, indicate that little chemical change has occurred to Tefzel in any of the Fluid F exposures employed. However, physical or physicochemical changes (i.e. loss of crystallinity, implicit removal of low molecular weight species) have taken place, although in a 'measured' fashion, i.e. no catastrophic deterioration has occurred.

An attempt was made to employ Q values from HP CH₄ permeation testing as a diagnostic tool for assessing effects of ageing. The exposure time required at each temperature to increase from the original 0.09cm²/s/atm to an empirically-chosen value of 0.15cm²/s/atm was used: those times were found always to associate with the second stage (above). The 100C value was obtained by interpolation, but times at the other two temperatures were read directly from Table 1. The ensuing line was good (Figure 5), and could perhaps be used for predictive purposes. The activation energy Ea (19kcal/mole) was apparently at the chemical level but, from the comments in the preceding paragraph, this is not likely. This point is now extended.

In the light of this apparent contradiction, the first stage modulus reductions at the different temperatures were re-examined by considering times to cause a 5% reduction in modulus rather than the longer times to reach the minima (as for Figure 4(a)). The resulting plot is shown in Figure 4(b); although there is some scatter, a representative line can be drawn, which gives an Ea of 29kcal/mole. This high value would normally be considered to associate with chemical mechanisms, but the analytical evidence here rules that out: however, there is one situation where an activation energy can be a summation of smaller Ea values, each arising from separate relevant processes, and this could apply here. Where there is an absolute interdependence between processes, for instance, permeation, diffusion and solubility coefficients (where Q=Ds), which each exhibit separate Arrhenius-type equations of identical form, the link can easily be shown. Writing the Arrhenius equations logarithmically, and substituting appropriately, it can be seen that

$$E_Q = E_D + E_S$$

Returning to the modulus/time plots, for the first stage, crystallinity loss itself causes modulus reduction, but *additionally* the extra amorphous region thus formed is a further

site for the gas absorption (a rapid process) which is also itself causing softening, i.e. the latter is linked with crystallinity level - the processes are interdependent.

Similarly with the E_a value of 19kcal/mole associated with the second stage (measured using CH_4 permeation as a diagnostic tool - see above) - as crystallinity becomes less through ageing, the increased amorphous volume would allow more loss of low molecular weight species, i.e. the latter is also linked with crystallinity magnitude. This process is concerned with stiffening, whereas the value of 29kcal/mole is associated with softening. It is interesting, but perhaps coincidental, that the difference in these E_a values (10kcal/mole) accords well with the E_a of 9kcal/mole measured by examining times to reach the modulus minima (Figure 4(a)) - these being the meeting points of the first and second stages.

3.2 Fluid G (methanol and 1% ethylene diamine)

As this fluid is 100% liquid, pressurisation was carried out with a liquid pump and all the testpieces were fully submerged.

Table 2 summarises Fluid G results obtained. Exposure at 120C gave a reduction in modulus with time, as shown also in Figure 6. No modulus increase at longer times (cf Fluid F results), and hence no minimum modulus values, have been observed up to 6 weeks. Yield strain had increased from the original value of 20%, to 30% after 6 weeks. Modulus etc behaviour at the other temperatures supported this trend, with one exception, the result after 12 weeks at 100C, which was higher than the 8 week value.

An Arrhenius plot based on times for modulus to decrease by 25% has been established (Figure 7). At 9.5kcal/mole, E_a is well below the 29kcal/mole found for this stage for Fluid F ageing. There is apparently no interdependence of crystalline level reduction and absorption level of methanol-based Fluid G. The higher solubility parameter of methanol compared with that for high pressure Fluid F means that its concentration into Tefzel is probably lower, and its diffusion rate is slower: softening by absorption is not a major factor here. Similarly, the greater solubility parameter difference could mean that less low molecular weight species is being removed by leaching with this fluid, to explain the long delay in the onset of the "second stage" stiffening..

Crystallinity of the 4 week aged samples apparently showed a massive drop to 1.7% from 26%. The one-off nature of this measured value means that it needs verifying with other similarly-aged samples.

HP methane permeation has increased after ageing in Fluid G, as it did for Tefzel after ageing in any of the fluids. Once again, permeation rate had nearly doubled. This tends to indicate the major effect of crystallinity loss, discussed as contributing for Fluid F.

No colour changes or cracking of Tefzel were observed such as those observed for Coflon in Fluid G. Hence again the inferences are that physicochemical effects, but not actual chemical changes, are associated with Fluid G exposures. However, it may be less controllable than for Fluid F, as steady decreases in mechanical properties have been observed.

3.3 Fluid I (aromatic oil)

The constituents of Fluid I and their relative proportions are: heptane/cyclohexane/toluene/1-propanol, 35/35/20/10 by volume.

Again testpieces were fully submerged in the liquid: all tests were conducted at 140C. However, as well as testing at 5000 psi 140C, one test cell was run at vapour pressure, *i.e.* a gap was left at the top of the cell which would be saturated with vapour at 140C: no extra hydraulic pressure was applied in this case.

A large reduction in modulus occurred after 2 weeks at 140C 5000 psi (Table 3), the samples having lost half of their original modulus. An increase in modulus occurred after the 10 week exposure, but this had decreased somewhat again after 30 weeks. At vapour pressure no measurement was taken at 2 weeks, but at 10 weeks an even greater loss in modulus was recorded compared to the 5000 psi case, and at 30 weeks the value was even lower. Some swelling of the sample was also observed in this vapour pressure case only; clearly the constraining hydraulic effect at 5000psi opposed the swelling somewhat.

At 10 weeks, the application of 8% strain made little difference to measured values.

Crystallinity again showed a large decrease falling from 26% to 9% after 10 weeks at 140C. Once again, no colour change was noted.

The value of crack resistance after 30 weeks at 140C was greater than the unaged value, in contrast to the modulus behaviour. (Strain again made little difference.) It is possible that crack growth resistance is dependent on the amorphous layer to a great extent, unlike tensile modulus etc, which would be governed by crystallinity considerations. Hence the limited absorption of the liquid Fluid I might have performed a crack blunting role, to increase crack resistance, whilst also contributing in a small way to the overall modulus reduction, the latter being dominated by crystallinity loss. (With a gaseous fluid (F), this observation was not made.)

HP permeation rate was increased even more by Fluid I exposures than by Fluids F and G, the effect increasing with exposure time. The maximum increase was over three-fold the unaged value. Reasons are probably those given before.

3.4 Fluids B (wet CH₄/CO₂) and A (methanol)

Because even those fluids considered to date (which are more chemically-aggressive than Fluids B and A) did not cause chemical deterioration of Tefzel, little change would be expected here. This conclusion is confirmed by the unchanging elemental analysis values and unaltered appearance of Tefzel in Fluids B and A.

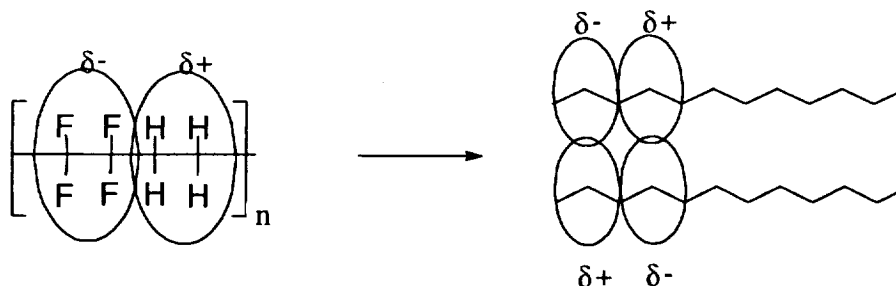
In both cases, modulus decreases with time were observed (presumably again due to crystallinity loss although appropriate values are not available). Comparison of the 2 week and 4 week modulus at 140C perhaps suggests that the loss of low molecular weight species is beginning to show for Fluid B. HP methane permeation results are again nearly doubled.

4 FURTHER DISCUSSION

To commence assessing the overall picture for Tefzel fluid exposures, although, as discussed below, solubility parameters δ are not major factors for this material - no common solvent dissolves Tefzel - nevertheless Fluid I with a δ value of $8.5 \text{ (cal/cm}^3)^{1/2}$ is seen to be more aggressive in swelling terms than methanol (δ 14.5), in contrast to the Coflon (δ 11.3) situation. Presumably the $-\text{CH}_2\text{CH}_2-$ groupings reduce δ compared with the Coflon value. Another interesting parallel for Tefzel (a TFE/ethylene copolymer) is the behaviour of the elastomer Aflas, a TFE/propylene copolymer, which swells up to 30% in hydrocarbons. The overall performance of Tefzel in the project fluids is apparently governed not by chemical reaction, but by resistance to physicochemical attack. Because in service the worst attack of this type would be by a main oilfield production fluid, another reason (besides explosive decompression) has therefore been shown for its lack of use in flexible pipes. Additionally, its successful employment with methanol in umbilicals can be understood: resistance to methanol at lower temperatures is good, and umbilicals would not be used at 140C where some Tefzel modulus decrease was seen with methanol (Fluid A). Even at this temperature there is no sign of the catastrophic deterioration which can be suffered by Coflon in methanol.

Turning to the mechanical and chemical stability of Tefzel, this can be attributed to several factors¹. If we compare the chemical structures of ETFE (Tefzel), and PTFE (Teflon) which is fully fluorinated, some of the reasons for the stability become apparent. Complete local substitution of some of the fluorine in PTFE by hydrogen in a regular alternating manner (pairs of atoms), to give ETFE, results in polarity, which leads to enhancement of mechanical properties. Polarity occurs because hydrogen has a different electronegativity compared to fluorine, and a different bond length to carbon. The centres of electronegativity and positivity *along* the polymer chain become unbalanced but can become more balanced *between* chains, given the correct alignment, see (1) below. No covalent bonds are broken in forming stabilised ETFE. Increased interaction between polymer chains results in increased mechanical properties compared to PTFE.

(1) Electron density distribution for ETFE

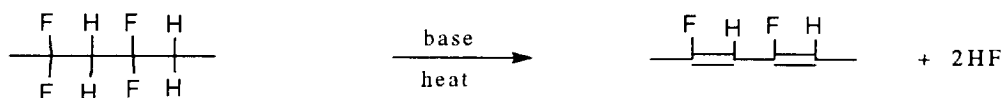


Intermolecular attractions. Extra stability.

Polarity and interpolymer chain attraction also cause high T_g values and influence resistance to fluid penetration into the amorphous regions of the polymer, explaining why Tefzel has no known solvent at ordinary conditions. Even with chemically-similar solvent (e.g. the solvent and Tefzel have similar solubility parameter values), the implied thermodynamic consequence of these interchain attractions is that entropy changes are kept to such an insignificant level that they even overrule the small enthalpic effects (arising from the similar solubility parameters) and thus avoid producing a negative free energy, and hence fluid absorption. (Similar effects for polymers generally can be obtained for other structural reasons, for instance chain crosslinking.)

These attributes for ETFE lead to chemical behaviour contrasting well with that of PVDF (Coflon) reported in CAPP/M.10. PVDF also contains hydrogen atoms, being an isomer of ETFE. However, its stoichiometry (arrangement of atoms) is such that its polymer chains will *not* align in the manner shown above: it does not possess extra stability from such intermolecular attractions. Several chemical mechanisms for Coflon deterioration are outlined in that report. The abundance of adjacent H and F atoms in PVDF leads to dehydrofluorination and formation of products based on the chemically stable conjugated molecule shown in (2) below.

(2) Conjugated PVDF degradation product



Other factors arising from the hypothesis¹ for the chemical stability of Tefzel, and, by implication, the potential for attack of Coflon, can be shown by considering project data. The stabilized structure for Tefzel in (1) means that double $\text{-CF}_2\text{CF}_2\text{-}$ groups align with analogous $\text{-CH}_2\text{CH}_2\text{-}$ groups on neighbouring chains - not the best arrangement for the occurrence of crystallization, which has been found to be at a level of only 26%, even when unaged. For Coflon, single $\text{-CF}_2\text{-}$ groups and $\text{-CH}_2\text{-}$ groups would align for interactive stability between chains: geometrically, however, only a small positional adjustment is required for each $\text{-CF}_2\text{-}$ group to align with another CF_2 group on an adjacent chain, so that crystallization can occur, but at the expense of interchain chemical stabilization. In this project, crystallinity levels of ~50% have been measured for Coflon. Hence the greater drive for crystallinity apparently reduces interchain chemical stability for Coflon, whilst the reverse is true for Tefzel. These basic tendencies influence the whole fabric of mechanical property, fluid absorption and chemical stability for the two polymers.

5 GENERAL CONCLUSIONS

- No evidence has been found from mechanical property, crack growth resistance, high pressure methane permeation, and chemical analysis tests for any chemical degradation of Tefzel during exposures to the project fluids at severe conditions.
- Intermolecular attractions between adjacent polymer chains are believed to account for the chemical stability of Tefzel as well as resulting in good mechanical behaviour. Reasons why these do not apply to Coflon, and possibly-related crystallinity aspects, have been discussed.
- Evidence has been found for physicochemical changes: reductions in crystallinity levels have been measured, and absorption of fluid and a loss of 2% of low molecular weight polymer have been implied by the data. Further X-ray diffraction data would be needed to verify whether loss in crystallinity can be correlated with any physical properties, but initial observations here indicate that this is quite likely.
- Modulus has been shown to fall to a minimum and then rise somewhat after exposure to Fluid F. Several Arrhenius plots have been established to bring out several features of its modulus/temperature relationship.
- Fluid G ageing has resulted in a gradual decline in modulus values during 120C exposures. Again, an Arrhenius plot has been developed.
- A large decrease in modulus has been observed during Fluid I exposures at 140C.
- Increased HP methane permeation through aged Tefzel has been attributed to increases in amorphous content and perhaps (i) loss of low molecular weight species leaving a microporous structure, (ii) minuscule damage due to explosive decompression. Fluid I caused a three-fold permeation increase, the other fluids can double the unaged rate: the rate also increases with exposure time and temperature.
- HP methane permeation has been used to give an Arrhenius plot which can compare ageing effects across temperatures. The magnitude of the activation energy for this plot, apparently at a chemical level, is more likely to arise from a combination of interdependent physicochemical processes.
- It is likely that the solubility parameter of Tefzel is lower than that of Coflon, so that aromatic oil (Fluid I) can be more aggressive than methanol to Tefzel, with the reverse true for Coflon.
- Modulus measurements may reflect crack growth resistance behaviour for HP gas exposures, but not liquid exposures. Crack growth resistance was increased after medium-term Fluid I ageing (unlike modulus).

ACKNOWLEDGEMENTS

This report is a resumé of data and ideas from all members of the CAPP project team at MERL and TRI. Sources of information are the CAPP technical reports, progress reports, meeting notes and personal discussions.

REFERENCE

- 1 J F Imbalzano, Basic Chemistry and Properties of Teflon/Tefzel, Technical Information Bulletin, Du Pont (USA)

TABLE 1 Test data - Tefzel aged in Fluid F(CH₄/CO₂/H₂S + 1% ethylene diamine in H₂O) at 5000psi, unstrained

| Sample & ageing history | Modulus | Yield stress | Yield strain | Ult strength | Ult strain | 70C crack growth resistance (J for 10nm/c) | CH ₄ perm'n coeff Q | Crystallinity | Elemental analysis | Visual appearance |
|-------------------------|---------|--------------|--------------|--------------|------------|---|---|---------------|--------------------|--------------------|
| Unaged | (MPa) | (MPa) | (%) | (MPa) | (%) | (kJ/m ²) | (cm ² /s/atm) x 10 ⁻⁶ | (%) | (%F) | |
| | 910 | 24 | 20 | 42 | 427 | 3.3 | 0.09 | 26.0 | 61 | Translucent, white |
| 2 months 85C | 927 | 27 | 18 | 42 | 402 | | | | | |
| 6 months 85C | 884 | 25 | 19 | 42 | 414 | | | | |) |
| 1 month 100C | 863 | 26 | 20 | >31 | >245 | | | 18.0 | 60 |) |
| 3 months 100C | 897 | 25 | 20 | >30 | >240 | | 0.14 | | |) |
| 6 months 100C | - | - | - | - | - | | 0.18 | | |) |
| 1 week 120C | 798 | 23 | 20 | 42 | 434 | | | | |) |
| 2 weeks 120C | 841 | 25 | 22 | >29 | >250 | | 0.12 | | |) Virtually |
| 3 weeks 120C | 775 | 22 | 20 | 39 | 414 | | | | |) unchanged |
| 4 weeks 120C | 811 | 26 | 20 | 39 | 369 | | 0.15 | 22.9 | 61 |) |
| 6 weeks 120C | 865 | 24 | 21 | 35 | 358 | | 0.07 | | |) |
| 3 days 140C | 790 | 23 | 23 | >30 | 244 | | | | |) |
| 5 days 140C | 737 | 23 | 25 | >30 | >250 | | | | |) |
| 8 days 140C | 714 | 23 | 24 | >27 | >250 | | 0.15 | 20.2 | 61 |) |
| 2 weeks 140C | 892 | 23 | 20 | 39 | 390 | | | | |) |
| 4 weeks 140C | 900 | 24 | 21 | 38 | 382 | 3.4 | 0.18 | | |) |

NB: Modulus etc from tensile measurements

CH₄ permeation at 150°C, 5kpsi: the unaged value is correct - an incorrect value was inadvertently included in the first issue of this report.

Unaged CH₄ concentration values (cm³ gas at STP/cm³ polymer) at 150C, 120C, 90C were 37, 24, 26 respectively.

TABLE 2 Test data - Tefzel aged in Fluid G (methanol + 1% ethylene diamine), unstrained at 5000psi unless indicated otherwise

| Sample & ageing history | Modulus (MPa) | Yield stress (MPa) | Yield strain (%) | Ult strength (MPa) | Ult strain (%) | CH ₄ perm'n coeff Q (cm ² /s/atm) x 10 ⁻⁶ | Crystallinity (%) | Visual appearance |
|---------------------------------|---------------|--------------------|------------------|--------------------|----------------|--|-------------------|-------------------|
| Unaged | 910 | 24 | 20 | 42 | 427 | 0.09 | 26.0 | White |
| 8 weeks 65C at vapour pressure | 897 | 26 | 20 | 45 | 458 | | |) |
| 26 weeks 65C at vapour pressure | 783 | 24 | 20 | 38 | 416 | | |) |
| 8 weeks 85C | 873 | 27 | 21 | 41 | 410 | | |) |
| 10 weeks 85C | 828 | 26 | 22 | 40 | 385 | | |) Slight |
| 12 weeks 85C | 773 | 26 | 25 | 41 | 398 | | |) discoloration |
| 6 weeks 100C | 803 | 26 | 25 | 41 | 391 | | |) |
| 8 weeks 100C | 797 | 26 | 23 | 39 | 414 | | |) |
| 12 weeks 100C | 864 | 27 | 22 | 39 | 372 | | |) |
| 2 weeks 120C | 804 | 23 | 21 | 39 | 399 | | |) |
| 4 weeks 120C | 805 | 25 | 24 | 41 | 448 | 0.15 | 1.7? |) |
| 6 weeks 120C | 755 | 24 | 30 | 41 | 466 | 0.18 | |) |

NB: Modulus etc from tensile measurements
CH₄ permeation at 150°C, 5kpsi

TABLE 3 Test data - Tefzel aged in Fluid I (heptane/cyclohexane/toluene/1-propanol), unstrained at 5000psi unless indicated otherwise

| Sample & ageing history | Modulus | Yield stress | Yield strain | Ult strength | Ult strain | 70C crack growth resistance (J for 10nm/c) | CH ₄ perm'n coeff Q | Crystallinity | Visual appearance |
|-------------------------------------|---------|--------------|--------------|--------------|------------|---|---|---------------|-------------------|
| | (MPa) | (MPa) | (%) | (MPa) | (%) | (kJ/m ²) | (cm ² /s/atm) x 10 ⁻⁶ | (%) | |
| Unaged | 910 | 24 | 20 | 42 | 427 | 3.3 | 0.09 | 26.0 | White |
| 2 weeks 140C | 444 | 19 | 54 | 28 | 256 | | - | |) |
| 10 weeks 140C | 551 | 19 | 25 | 30 | 333 | | 0.23 | 9 |) |
| 10 weeks 140C 8% tensile strain | 583 | 19 | 21 | 36 | 433 | | | |) |
| 10 weeks 140C at vap pressure | 517 | 18 | 26 | 29 | 351 | | | |) Unchanged |
| 30 weeks 140C | 518 | 20 | 42 | 30 | 341 | 4.2* | 0.30 | - |) |
| 30 weeks 140C at vapour pressure | 494 | 20 | 35 | 30 | 350 | | | |) |

NB: Modulus etc from tensile measurements

CH₄ permeation at 150°C, 5kpsi

* When tested strained at the same conditions, crack growth resistance = 4.0

TABLE 4 Test data - Tefzel aged in Fluid B (methane, carbon dioxide, with saturated water vapour) at 5000psi

| Sample & ageing history | Modulus (MPa) | Yield stress (MPa) | Yield strain (%) | Ult strength (MPa) | Ult strain (%) | CH ₄ perm'n coeff Q (cm ² /s/atm) x 10 ⁻⁶ | Crystallinity (%) | Elemental analysis (%F) | Visual appearance etc |
|-------------------------|---------------|--------------------|------------------|--------------------|----------------|--|-------------------|-------------------------|-----------------------|
| Unaged | 910 | 24 | 20 | 42 | 427 | 0.09 | 26.0 | 61 | Translucent, white |
| 12 weeks 90C | 772 | 24 | 21 | 34 | 357 | | | |) |
| 4 weeks 120C | 800 | 23 | 21 | 38 | 400 | | | |) |
| 12 weeks 120C | 745 | 24 | 21 | 38 | 400 | | | |) No change |
| 2 weeks 140C | 798 | 23 | 21 | 36 | 379 | 0.16 | | 61 |) |
| 4 weeks 140C | 800 | 22 | 21 | 36 | 388 | | | |) |
| | | | | | | | | |) |
| | | | | | | | | |) |

NB: Modulus etc from tensile measurements
CH₄ permeation at 150°C, 5kpsi

TABLE 5 Test data - Tefzel aged in Fluid A (methanol), unstrained at 5000psi unless otherwise indicated

| Sample & ageing history | Modulus (MPa) | Yield stress (MPa) | Yield strain (%) | Ult strength (MPa) | Ult strain (%) | CH ₄ perm'n coeff Q (cm ² /s/atm) x 10 ⁻⁶ | Crystallinity (%) | Elemental analysis (%F) | Visual appearance etc |
|----------------------------------|---------------|--------------------|------------------|--------------------|----------------|--|-------------------|-------------------------|-----------------------|
| Unaged | 910 | 24 | 20 | 42 | 427 | 0.09 | 26.0 | 61 | Translucent, white |
| 6 days 140C at vapour pressure | - | - | - | - | - | - | 25.6 | | |
| 8 days 140C | 862 | 26 | 22 | 38 | 350 | | | 61 |) |
| 14 days 140C | 715 | 24 | 20 | 35 | 351 | | | |) Unchanged |
| 14 days 140C 3% tensile strain | 700 | 24 | 20 | 38 | 384 | | | |) |
| 14 days 140C 7.5% tensile strain | 670 | 26 | 22 | 36 | 327 | 0.15* | | |) |

NB: Modulus etc from tensile measurements

CH₄ permeation at 150°C, 5kpsi

The diffusion coefficient at 150C for Fluid A ingress into unaged Tefzel is 0.25x10⁻⁶cm²/s

* Aged at 150C

FIGURE 1: Change in modulus of Tefzel exposed to Fluid F at 100°C

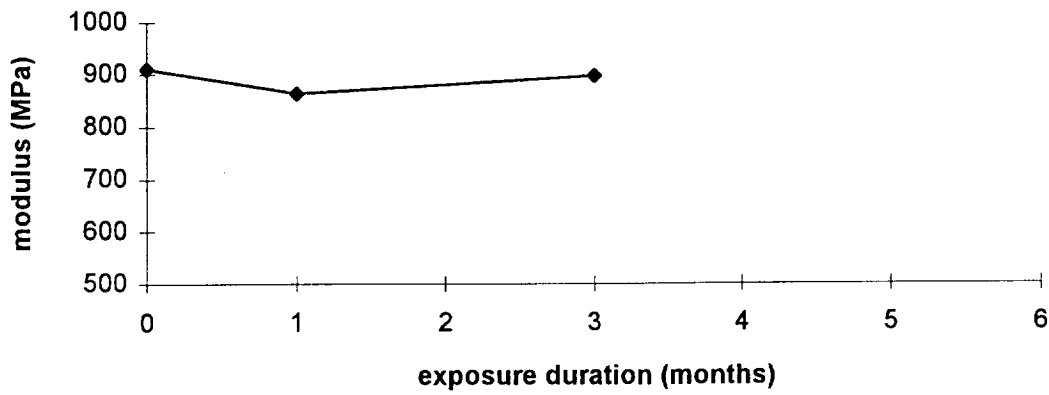


FIGURE 2: Change in modulus of Tefzel exposed to Fluid F at 120°C

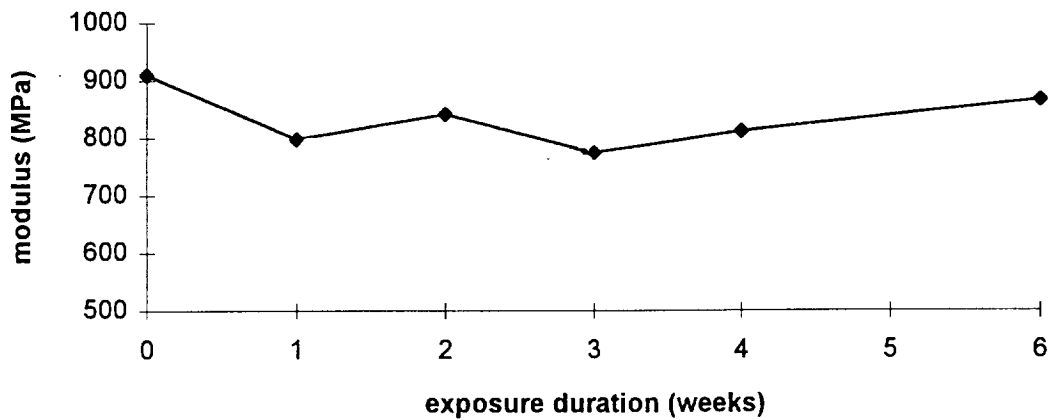
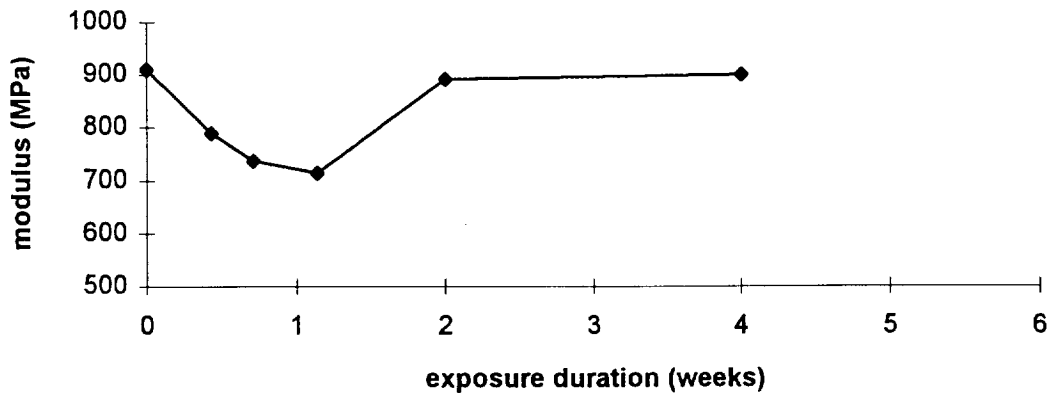
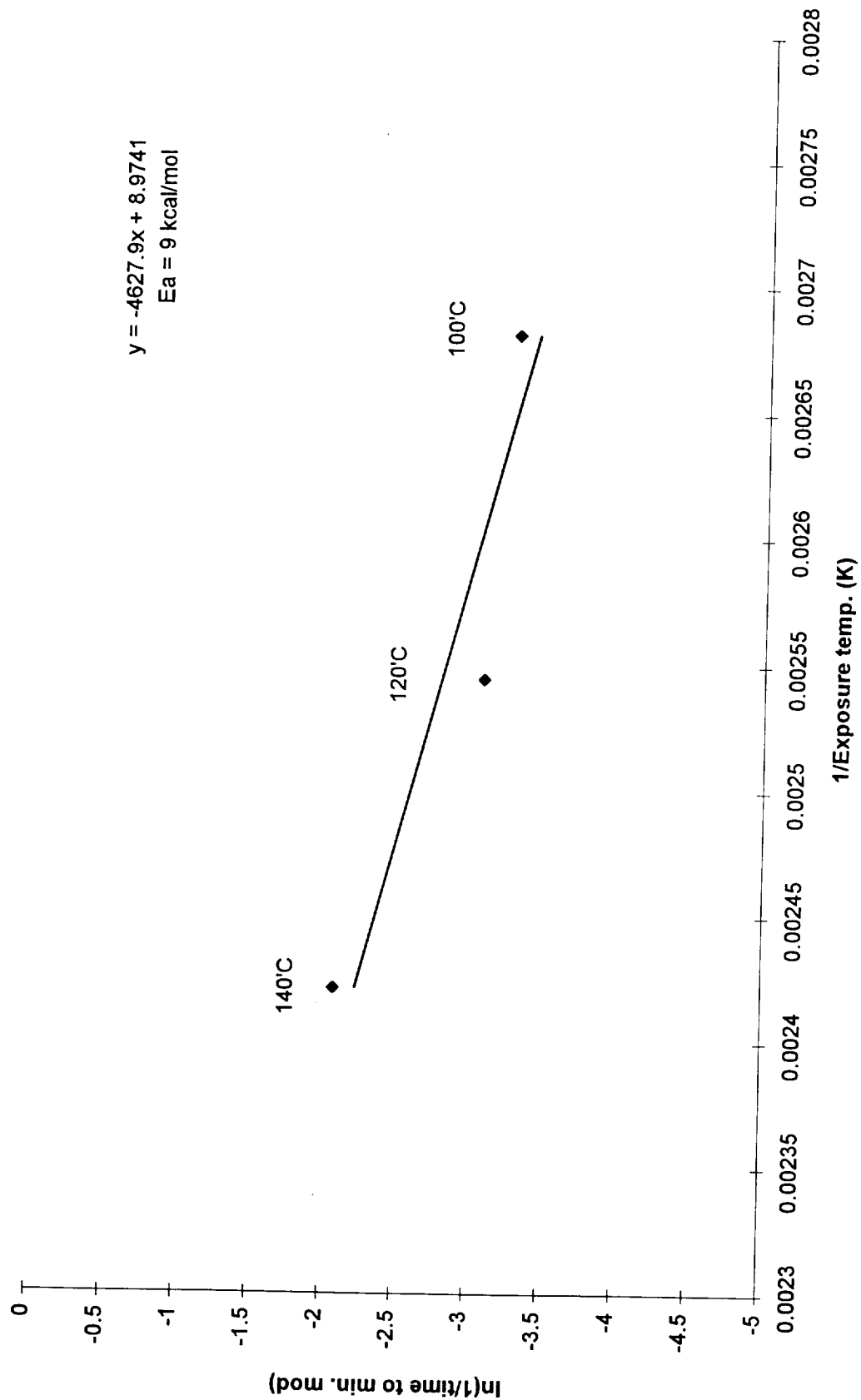


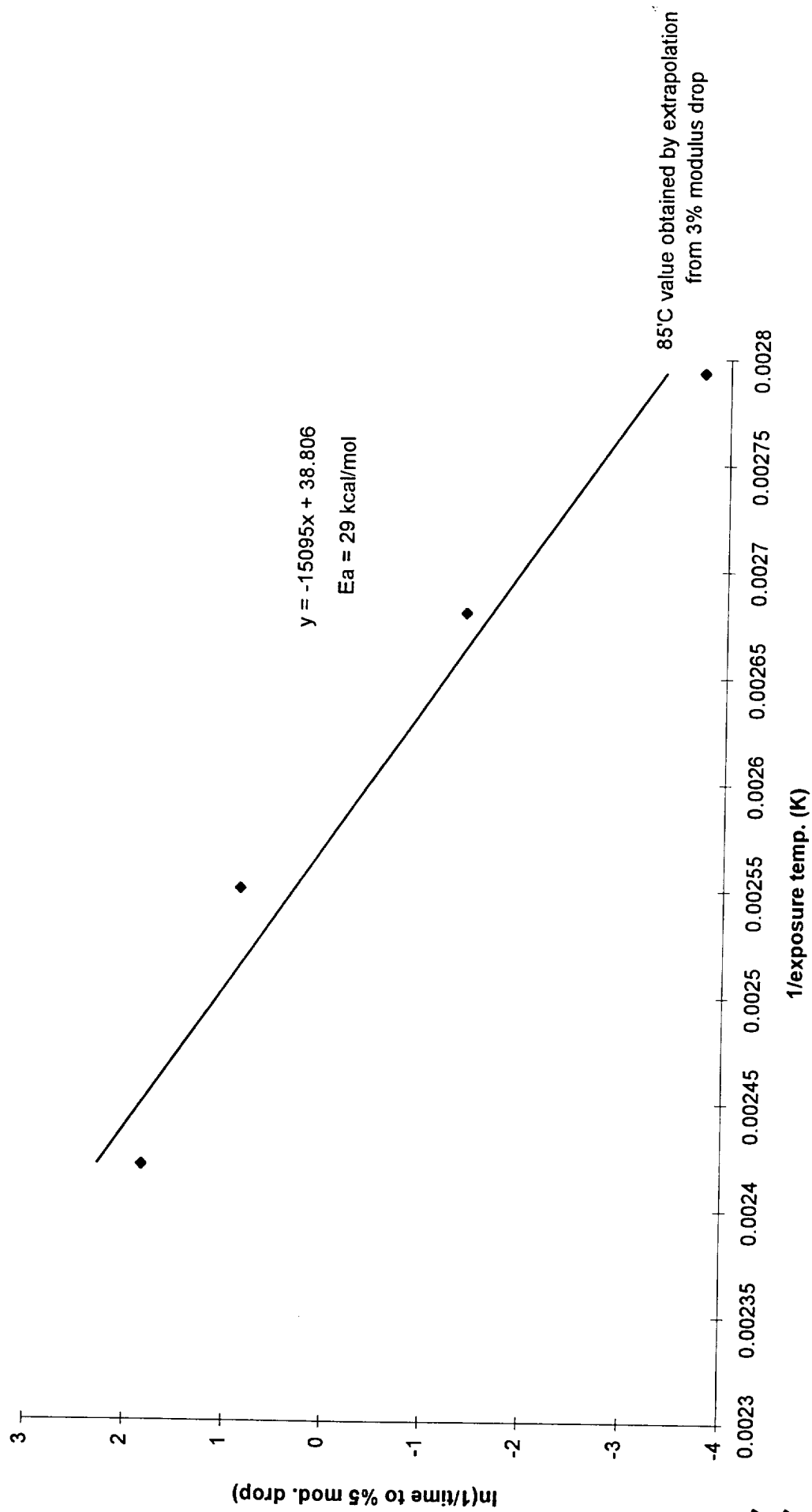
FIGURE 3: Change in modulus of Tefzel exposed to Fluid F at 140°C



**FIGURE 4(a): Arrhenius plot of time to minimum modulus
after Fluid F exposure of Tefzel**



**FIGURE 4(b): Arrhenius plot of time to 5% modulus drop
after Fluid F exposure of Tefzel**



**FIGURE 5: Arrhenius plot for methane permeation through Tefzel
after Fluid F ageing**

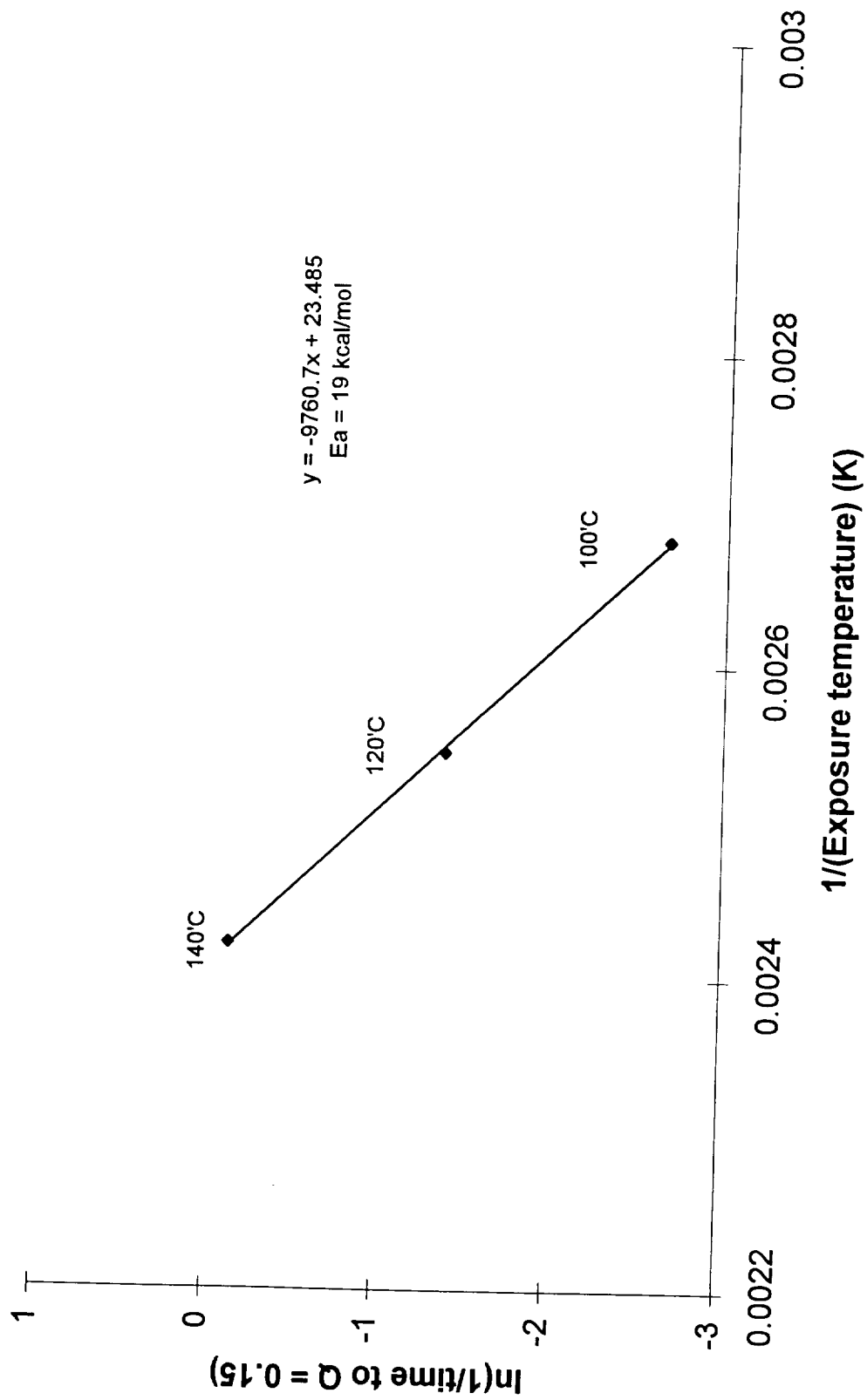
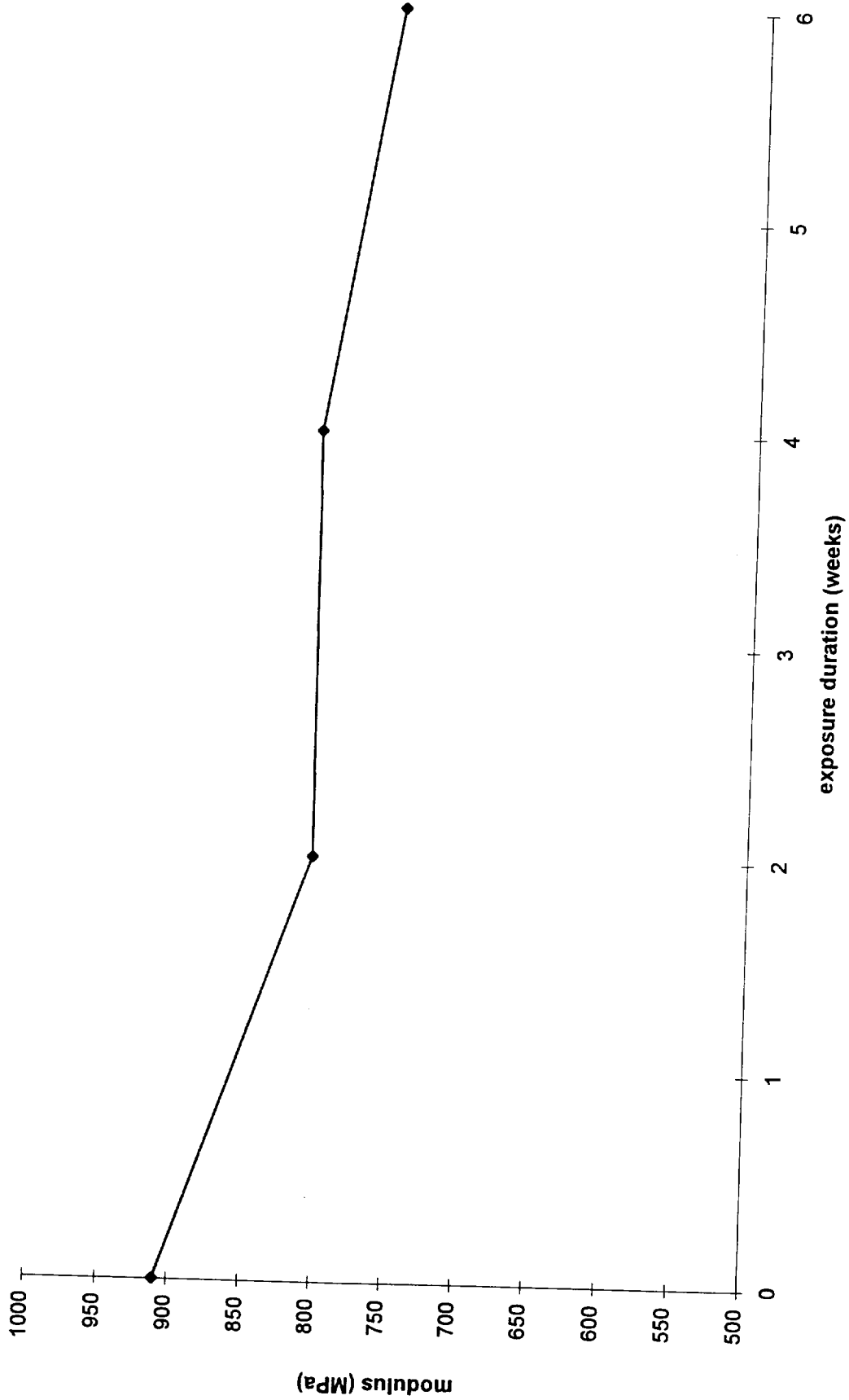


FIGURE 6: Change in modulus of Tefzel exposed to Fluid G at 120°C



**FIGURE 7: Arrhenius plot of time to 11.5% drop in modulus
after Fluid G exposure of Tefzel**

